Passive Sampling Devices: A Cost-Effective Method of Obtaining Air Quality Data in Protected Areas

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1.0 Introduction

The U.S. National Park Service (U.S. NPS) has as its mission the conservation of its natural and cultural resources in its national parks for the enjoyment of current and future generations. In addition, the Park Service has an affirmative responsibility under the U.S. Clean Air Act to protect its natural resources from the adverse effects of air pollution.[1] The U.S. Clean Air Act also established a national visibility protection goal to eliminate existing and prevent future visibility impairment in specially designated areas, known as Class I areas, in the United States.[2] These class I areas include national parks and wilderness areas administered by the U.S. National Park Service, the U.S. Fish and Wildlife Service, and the U.S. Forest Service. There are currently 158 class I areas in the U.S., 48 of which are administered by the U.S. NPS. A critical component of the Park Service's air resource management program is the measurement of air quality in its parks. In fact, one of the U.S. NPS servicewide goals recently established as part of the Government Performance and Results Act relates to the improvement, or at least no degradation, of air quality in its parks. [3]

Since the late 1970s the U.S. National Park Service has maintained an air quality monitoring network in national parks. Measurements for visibility, precipitation chemistry, fine particles, gaseous pollutants, and meteorology have been made in 76 NPS units since that time. The current number of NPS units with air quality monitoring network (Figure 1) are: 18 with optical (transmissometer or nephelometer) monitoring; 37 with fine particle (particles with diameter less than or equal to 2.5 micrometers) monitoring; 4 with photographic (35 mm camera) monitoring; 31 with ozone monitoring; and 29 with precipitation chemistry monitoring. U.S. NPS air quality monitoring and research costs for the 1997 fiscal year will be approximately $3.29 million, accounting for approximately 60% of the U.S. NPS Air Resources Division's budget. Since about 1989, however, the funding available to maintain these programs has gradually diminished due to inflation and growing personnel costs. In order to acquire the information necessary to guide air resource management decisions it is often necessary to develop and use lower cost monitoring methods. This paper discusses one of the efforts currently being employed by the U.S. NPS in meeting its air quality data requirements.

2.0 NPS Monitoring Strategy

In 1991, the U.S. NPS developed a monitoring strategy for the measurement of gaseous pollutants in parks. This strategy called for the continued measurement of gaseous air pollutants in parks, primarily in parks designated as Class I areas. Under this strategy, two types of sites would be established: baseline and trend. Trend sites are intended to be maintained indefinitely to provide sufficient information to assess long-term trends in air quality. The network of trend sites was established to represent each of the major ecological regions in which NPS had significant acreage, and the number of sites in each ecological region was proportionally allocated based on the amount of NPS acreage in an ecoregion. The intent of the baseline sites is to establish existing conditions at all other NPS class I areas which were not included as part of the trend network. The strategy called for an initial measurement period at these baseline sites of 3 to 5 years after which time monitoring would not re-occur for a period of 5 to 7 years. A total of 32 parks would be monitored at any given time (24 trend sites plus 8 baseline sites). The strategy also called for the development and testing of low-cost methods to meet NPS air quality data needs, at least with respect to the measurement of gaseous air pollutants--ozone, sulfur dioxide and nitrogen oxides.

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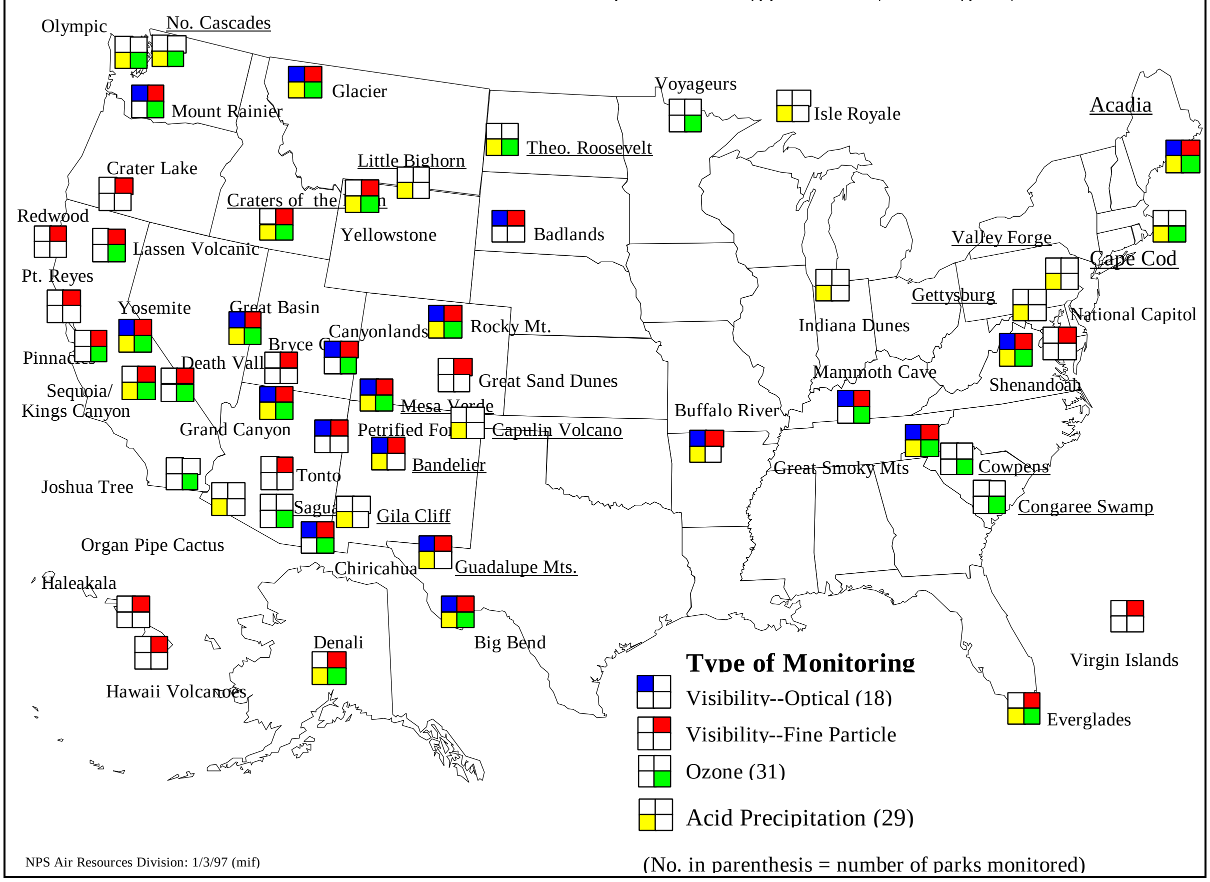
1 42 U.S.C. 7401 et seq., Section 165
2 42 U.S.C. 7401 et seq., Section 169A
3 National Park Service Strategic Plan, Final Draft, 1996, NPS D-1151, September 1996.

Figure 1

Air Quality Monitoring in U.S. National Parks, by Type

Parks in underline indicates partial funding provided by other agency



3.0 Ozone and Its Measurement

Tropospheric ozone is the most pervasive air pollutant in the U.S. Not only does ozone cause significant health effects when present at sufficiently high levels (0.08 ppm to 0.12 ppm), it is also known to be phytotoxic. In November 1996 the US Environmental Protection Agency proposed revisions to the National Ambient Air Quality Standards for ozone. Included in this proposal was a secondary standard to be protective of vegetative effects such as visible foliar injury, growth reductions and yield loss in annual crops, growth reduction in tree seedlings and mature trees, and effects that can have impacts at the forest stand and ecosystem level.[4] In this proposal, EPA cited several studies conducted in national parks and national forests in the US.

Because of the potentially damaging effects of ozone and other gaseous pollutants to many of the resources found in our national parks, the U.S. NPS has maintained an extensive network of ozone continuous monitoring stations that operate year-round. At one time as many as 42 stations were operating in parks. These stations are equipped with UV photometric analyzers for the continuous measurement of ozone and are linked to a centralized database via telephone service. Each station is polled nightly and the data are downloaded to a centralized computer to begin the data validation process. U.S. Environmental Protection Agency (U.S. EPA) monitoring protocols require the ozone analyzers to be maintained in

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[4] *Environment Reporter*, Bureau of National Affairs, Inc. Vol. 27, No. 32, December 13, 1996, pp. 1672-1720.

temperature-controlled shelters at 20° to 30° Celsius[5] , which add significant costs to the monitoring effort. The annual costs to maintain an ozone monitoring station equipped with a 10-meter meteorological tower can range from $25,000 to $60,000, or higher depending on the organization conducting the monitoring, the number of field site visits, data capture requirements and other factors.

3.0 Using Passive Samplers for Ecological Monitoring

The use of passive devices for ecological monitoring purposes is not new.[6] Passive sampling devices rely on the principle of air diffusion and the air coming in contact with a reactive agent. Because these devices have no moving parts, their costs are very low when compared to the cost of a continuous analyzer. Because passive sampling devices require no AC line power as do the continuous analyzers, these devices can be deployed virtually anywhere thus making them ideal for ecological monitoring in remote areas. The majority of the cost associated with the use of passive samplers is the cost of laboratory sample analysis. A comparison of the typical costs associated with passive samplers and continuous analyzers is presented in Table 1, assuming a 5-month operation during the typical "ozone season" in the US (May-September). As can be seen from this table the use of passive sampling devices can result in significant savings. The operation of the device relies on ozone diffusing into the sampler and coming into contact with a chemically impregnated filter that reacts with ozone. Once the sampler has been exposed for the desired duration, it is sent to a laboratory where the filter is chemically analyzed. Capital and installation costs are non-recurring, and because the passive samplers are reusable, annual recurring costs are approximately US$ 1,400 for passive sampling v. US$ 20,000 for continuous monitoring.

Costs (in US Dollars)	**Passive Sampler**	**Continuous Analyzer**
Capital	$ 942	$ 40,000
Installation	30	20,000
Operation	15	13,000
Sample Analysis	950	0
Supplies	5	800
Data Processing and Validation	70	2,000
Quality Control/Quality Assurance[7]	322	2,500
Total	**$ 2,334**	**$ 78,300**

Table 1. Comparison of costs between passive sampling devices (weekly sampling) and continuous analyzers for the measurement of ozone at one location.

4.0 Use of Ozone Passive Samplers in U.S. National Parks

In 1991 the U.S. NPS conducted an initial experiment to test the feasibility of using these devices in national parks. To conduct this experiment, the NPS selected the Ogawa passive sampler that was originally manufactured as a personal exposure monitor for nitrogen oxides and had been modified by Harvard University researchers for ozone monitoring[8]. The device is constructed of Teflon® and is cylindrically shaped with an outside body diameter of 19 mm, a length of 30 mm, and weight of 10 grams (see Figure 2). Two 14.5 mm diameter filters impregnated with a nitrite solution are held in place on each end of the sampler by end caps with holes that allow air to diffuse into the sampler. Ozone reacts with the nitrite to form nitrate that is then analyzed in the laboratory using ion chromatography. The

[5] 40 CFR 58, Appendix A and B

[6] Mulik, J D *et. al.*, "Using Passive Sampling Devices to Measure Air Volatiles for Assessing Ecological Change", in Proceedings of the 1991 U.S. EPA-AWMA International Symposium on Measurement of Toxic and Related Air Pollutants, VIP-21, Air & Waste Management Assoc., Pittsburgh, 1991, pp. 285-290.

[7] Quality control for a continuous analyzer requires the use of an ozone generator and separate UV photometer (usually one unit) to conduct periodic zero, span, and precision checks and multi-point calibrations. Quality assurance of continuous analyzers requires field audits performed using independent equipment and auditors for the assessment of instrument accuracy.

[8] Koutrakis, P *et al.*, "Measurement of Ozone Exposures" in Proceedings of the 1990 U.S. EPA-AWMA International Symposium on Measurement of Toxic and Related Air Pollutants, VIP-17, Air & Waste Management Assoc., Pittsburgh, 1990, pp. 468-474.

samplers must be contained in a rain shield to avoid nitrate in rainwater from contaminating the sample. Duplicate samplers are used at each location to obtain information on sampling precision.

Passive sampler photograph

An elaborate experimental design was developed to test these devices at locations with continuous ozone analyzers for various sampling durations ranging from 1 week to 8 weeks and for a range of environmental factors that could influence the results (e.g., high/low ozone exposures, high/low elevations, and high/low relative humidity). Unfortunately, the rain shields used to protect the sampler from rain (hence, artifact formation) were constructed of translucent, polypropylene materials, which for some unknown reason may have contaminated the samples. Also, the coating on the filters was increased proportionally to sampling duration (e.g., the nitrite solution used to impregnate filters to be used for 4-week sampling was 4 times that of the 1-week sample), something that had not been tested previously. The results of this experiment exceeded the desired ± 20% accuracy goal. In 1993, NPS switched to rain shields constructed of PVC materials and chose a sampling duration of 1 week. Tests were performed at 3 locations prior to deployment in the field to confirm that the new rain shields would yield acceptable results. Following this preliminary trial, samplers were deployed at five locations in 2 parks co-located with continuous analyzers. The results showed that passive samplers agreed with weekly average ozone concentrations obtained using continuous analyzers within ± 20%. The 95% confidence interval on precision (or reproducibility of the passive sampling measurement), as determined by duplicate samples, was ± 0.5 part per billion (ppb).[9]

Because ozone passive sampling had been found to be sufficiently reliable and because funding shortfalls would not allow the ozone monitoring at previously designated NPS baseline sites using continuous analyzers, NPS began using passive samplers at parks that had been designated as baseline sites on a more routine basis in 1995 (14 locations) and 1996 (17 locations). In addition, ozone spatial distribution studies using numerous passive sampling locations have been conducted in 6 national parks.

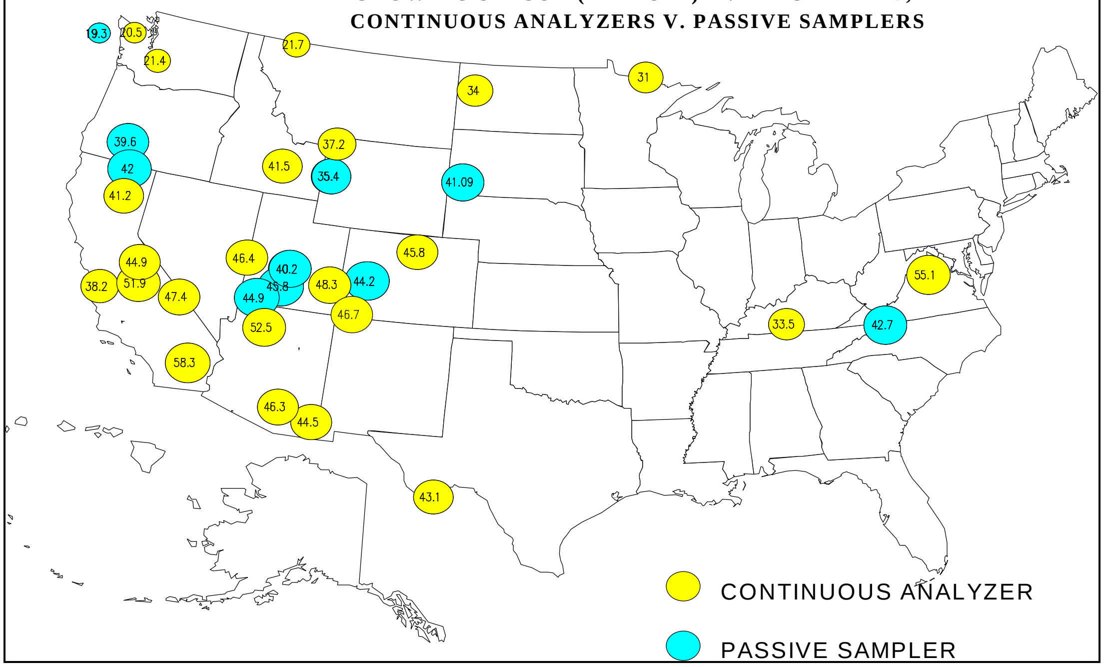
4.1 1995 and 1996 Ozone Passive Sampling Results

Figures 3 and 4 show a comparison of passive sampling and continuous monitoring results for ozone in national parks for the period May through September, 1995 and 1996.

[9] Ray , J D and Flores, M I. "Evaluation of Passive Samplers for Field Measurements of Ambient Ozone in the National Parks", in Proceedings of the 1994 U.S. EPA-AWMA International Symposium on Measurement of Toxic and Related Air Pollutants, VIP-39, Air & Waste Management Assoc., Pittsburgh, 1994, pp. 418-421.

Figure 3.

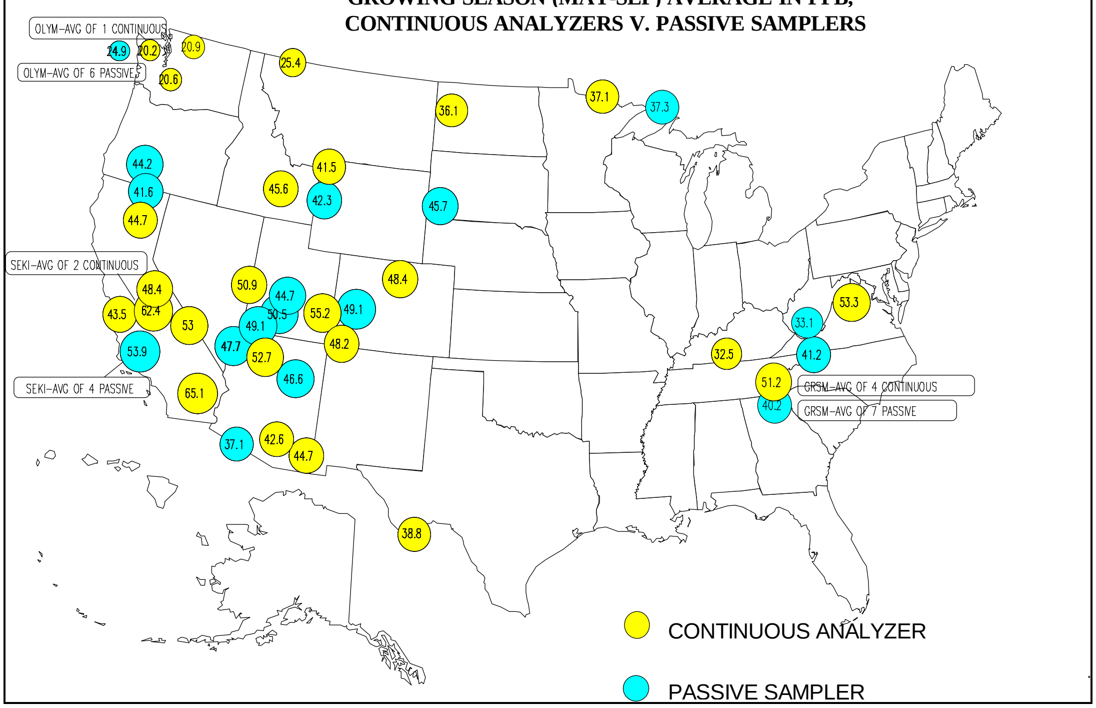
1995 OZONE CONCENTRATIONS IN U.S. NATIONAL PARKS, GROWING SEASON (MAY-SEP) AVERAGE IN PPB, CONTINUOUS ANALYZERS V. PASSIVE SAMPLERS



The seasonal average ozone concentration at passive sampling locations appear to be very consistent with the data obtained from continuous analyzers. A similarly consistent comparison in 1996 is equally apparent from Figure 4.

Figure 4.

1996 OZONE CONCENTRATIONS IN U.S. NATIONAL PARKS, GROWING SEASON (MAY-SEP) AVERAGE IN PPB, CONTINUOUS ANALYZERS V. PASSIVE SAMPLERS



Although a rigorous statistical analysis of these results is planned, the US NPS is satisfied that ozone passive samplers can be used to obtain estimates of ozone concentrations and exposures in parks not previously monitored. In addition to filling in data gaps and establishing ozone levels in parks, passive samplers can be used at multiple locations within a park to determine locations of higher ozone exposures and determine the spatial gradient of ozone concentrations. This is particularly beneficial in areas with complex terrain where ozone concentrations could be considerably different from one side of the park to the other. An example of this use is illustrated in Figure 5 showing the results of 5 passive sampling sites and one continuous analyzer site at Olympic National Park in 1996.

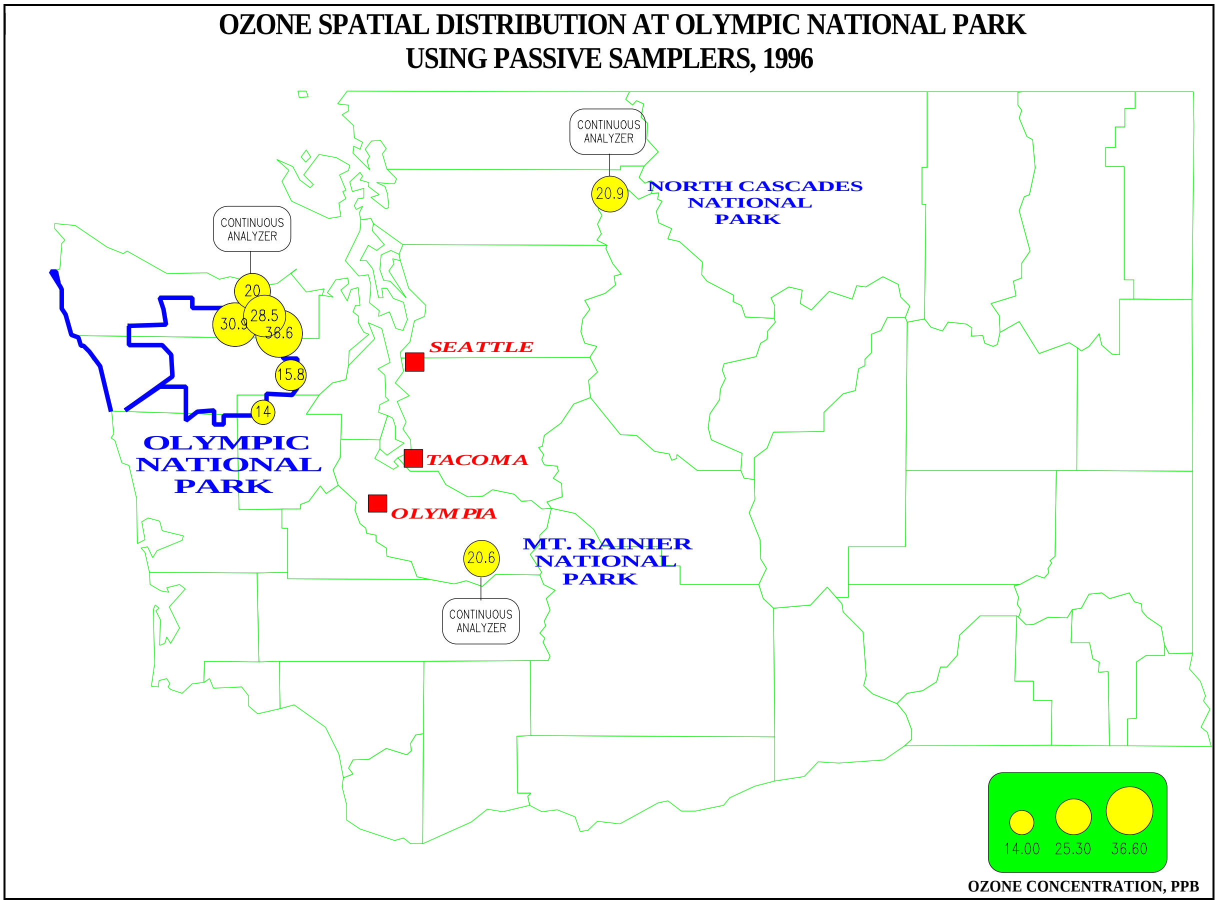


Figure 5. Average ozone concentrations determined by passive samplers at Washington State NPS sites.

The results clearly indicate that measurements made at the continuous monitoring location at a low elevation just south of the town of Port Angeles, Washington, is not sufficient to characterize ozone exposures in the park. Locations at higher elevations and on the east side of the park northeast of the Seattle metropolitan area receive a much greater ozone exposure than do other locations. Surprisingly, sampling locations in the southeastern part of the park that were in lower elevation but downwind of the Olympia-Tacoma area with southeasterly flows, were much lower than the northern region.

4.2 Uses and Limitations of Passive Sampling

Several uses of passive sampling devices have been presented. In addition to establishing current ozone exposures in areas and performing spatial gradient studies, the devices can be used at biomonitoring plot locations to relate observed ozone injury to vegetative species to an actual ozone exposure. Passive samplers can also be used to assess how representative a fixed, continuous monitoring location can be of ozone levels in surrounding biomonitoring plots. The US NPS has also used the devices to obtain ozone gradient information within a forest canopy, finding much higher ozone levels near the top of the tree canopy. There appear to be endless uses of passive devices for ecological monitoring purposes.

There are, however, some limitations in the use of the data obtained from passive samplers. Because the passive sampler provides an integrated measurement over time, usually one-week, no information is obtained regarding the diurnal pattern at the monitoring location. Sometimes this might be of interest. Analysis of hourly averaged ozone concentrations obtained in US national parks show a clear diurnal pattern that varies with elevation. Lower elevation sites have a more pronounced diurnal variation with ozone concentrations in the early morning and late evening hours being much lower than peak concentrations that typically occur in mid to late afternoon. Higher elevation sites have a much less pronounced pattern, oftentimes with ozone concentrations remaining fairly constant throughout the day and night. Although there may be methods of estimating the peak hourly concentration from weekly integrated measurements by assuming the measurements can be well approximated by a probability density function such as the lognormal distribution, the actual daily diurnal pattern of ozone concentrations cannot likely be estimated from weekly integrated measurements. This requires further study. In not all cases will the weekly exposure, or SUM0, be the appropriate statistic that relates best to observed vegetative effects. As mentioned previously, the US EPA recently proposed an ozone secondary standard. This proposed secondary standard is based on the SUM06 statistic. SUM06 is calculated by summing all hourly ozone concentrations that exceed 0.06 parts per million (ppm), or 60 ppb. Data obtained from passive samplers could not easily be used to assess the likelihood of an area being out of compliance with such a standard.

5.0 Conclusions

The US National Park Service has used passive sampling devices for the routine measurement of ozone in national parks since 1995. Results indicate that the accuracy of these devices when compared to co-located continuous ozone analyzers is ± 15% with a repeatability of the measurement (precision) of ± 1% (relative standard deviation). When compared to the use of continuous methods, the use of passive sampling devices can be very cost effective, with costs of approximately $2,300 per site for a 5-month sampling period. Although there are limitations in the use of weekly integrated measurements obtained with passive sampling devices, the potential uses of these devices for ecological monitoring purposes far outweigh these limitations. Passive sampling devices provide resource managers with a lower cost alternative in performing air quality monitoring for ecological purposes in protected areas. Because of their utility, ease of operation, and low cost, the US NPS has begun the use of these devices for the measurement of other gaseous pollutants, such as sulfur dioxide, nitrogen oxide, and nitrogen dioxide.